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14. ABSTRACT
The United States Air Force School of Aerospace Medicine's Consultative Services Division (USAFSAM/OEC) was asked by HQ ACC/SGXH to evaluate the TVA-1000B toxic vapor analyzer due to the fact that its life cycle as standard Air Force Bioenvironmental Engineering equipment is projected to end in 2014. The primary purpose of the TVA-1000B is to provide a quick screening tool for detection of a wide variety of toxic industrial chemicals/materials, while at the same time giving a good approximation of the quantity of contaminant present. USAFSAM was asked to determine whether a commercial off-the-shelf (COTS) solution exists that could better detect and quantify a broader range of chemicals than the TVA-1000B. USAFSAM conducted an exhaustive literature review to answer this question. Based on this review, there do not seem to be enough significant advantages in existing COTS portable gas and vapor monitoring instruments to justify replacing the TVA-1000B at this time.

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DEPARTMENT OF THE AIR FORCE
USAF SCHOOL OF AEROSPACE MEDICINE (AFMC)
WRIGHT-PATTERSON AFB OH

22 May 2013

MEMORANDUM FOR HQ ACC/SGXH
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SUBJECT: Consultative Letter AFRL-SA-WP-CL-2013-0012, Evaluation of TVA-1000B Toxic Vapor Analyzer

1. INTRODUCTION:

a. *Purpose*: In August 2012, the United States Air Force School of Aerospace Medicine's Consultative Services Division (USAFSAM/OEC) was asked by HQ ACC/SGXH to evaluate the TVA-1000B toxic vapor analyzer due to the fact that its life cycle as standard Air Force (AF) Bioenvironmental Engineering (BE) equipment is projected to end in 2014. The primary purpose of the TVA-1000B is to provide a quick screening tool for detection of a wide variety of toxic industrial chemicals/materials (TIC/TIM), while at the same time giving a good approximation of the quantity of contaminant present. USAFSAM was asked to determine whether a commercial off-the-shelf (COTS) solution exists that could better detect and quantify a broader range of chemicals than the TVA-1000B. USAFSAM conducted an exhaustive literature review to answer this question. The literature review identified three possible instruments that could replace the TVA-1000B: the MicroFID, ppbRAE, and MIRAN SapphIRe. Based on this review, there do not seem to be enough significant advantages in existing COTS portable gas and vapor monitoring instruments to justify replacing the TVA-1000B at this time.

b. *Background:*

(1) Photoionization Detector (PID): The PID uses high-energy ultraviolet light to excite gas or vapor molecules, causing the loss of an electron and the creation of a positively charged ion. The ions formed are then propelled in one direction by a bias electrode and accumulated at a collecting electrode; the ion current generated is amplified, then translated to a meter reading. A typical direct-reading portable PID displays readings in parts per million air concentration and the output value is related to the actual air concentration by calibration in a known atmosphere.[1] The common components of air (e.g., nitrogen, oxygen, helium, carbon dioxide, and water vapor) all have ionization potential (IP) higher than the energy of a typical PID lamp and so are

not ionized and are not detected. However, these compounds can cause ultraviolet radiation from the lamp to be scattered and absorbed. This is sometimes referred to as “quenching” because it attenuates the effective PID signal. Quenching gases include water vapor, carbon dioxide, methane, and carbon monoxide.[2] To effectively use a PID, the operator must know the IP of the chemicals suspected of being present in the air and the energy of the lamp in the PID. Furthermore, it is possible to use a PID quantitatively if only one chemical is present in air or if a mixture of chemicals is present and each chemical has the same IP. A PID can detect a range of organic chemicals and some inorganic chemicals including aromatics, unsaturated chlorinated hydrocarbons, aldehydes, ketones, ethylene oxide, hydrogen sulfide, and glycol ether solvents.[3] Some important chemicals cannot be detected by a PID, including hydrogen cyanide (which is detected by a flame ionization detector) and chlorine gas.[2]

(2) Flame Ionization Detector (FID): The FID is insensitive to most inorganic compounds, such as water, nitrogen, and oxygen, and its response to carbon monoxide and carbon dioxide is negligible, making it extremely useful for air sampling and analysis. FID response does not represent the concentrations of individual organic compounds, but rather an estimate of the combined concentration of volatile organic compounds present. If only one organic contaminant is present, it may be possible to quantify the contaminant if the FID has been calibrated for that specific contaminant. The reason for this limitation is that, although FID response is proportional to concentration, the relationship is not linear and is further skewed by organic compounds containing oxygen, nitrogen, sulfur, or chlorine.[3]

(3) Infrared (IR) Spectrometry: A third method of analysis of gases and vapors is IR spectrometry. Chemicals absorb infrared radiation at characteristic wavelengths and resonate at specific vibration frequencies. Because each type of molecular bond vibrates at a characteristic wavelength, if a molecule is exposed to electromagnetic energy at that wavelength, some of the energy is absorbed by the bond as it resonates. Because most chemicals have multiple types of bonds, they also often have multiple absorption wavelengths. The software in an IR instrument detects the presence of chemicals by monitoring one specific wavelength, a set of wavelengths, or an entire spectrum. The energy intensity at the correct wavelength(s) is used by the instrument to derive the contaminant concentration.[4]

2. LITERATURE REVIEW:

a. *TVA-1000B*: The TVA-1000B (Figure 1) is a direct-reading portable monitoring instrument that uses an FID, a PID, or both simultaneously to provide real-time measurements of the concentrations of many organic and some inorganic vapors in air. It can aid in quantifying known TIC/TIMs, but it does not identify the specific TIC/TIM present. It is not sensitive enough for use in detection and monitoring of chemical warfare (CW) agents. It does not have the capability to monitor or detect biological warfare agents or radiological hazards (*Final Guidance Document for Use of the Thermo Electron TVA-1000B Toxic Vapor Analyzer*; USAFSAM, 2007). A recent study by Coffey et al.[5] found that the TVA-1000B FID did not give any false negative readings during testing. Its performance was also not affected by relative humidity. The TVA-1000B PID, however, gave several false negatives and its performance was negatively affected by high humidity.[5] The TVA-1000B is the only existing COTS portable instrument that combines PID and FID technology in a single unit. The only way these two

technologies could otherwise be employed together is to use an instrument that contains a PID and a separate instrument that uses an FID.

Figure 1: Thermo Scientific TVA-1000B toxic vapor analyzer

b. *FIDs*: The MicroFID (Figure 2) by Photovac is a handheld portable FID, similar to the TVA-1000B FID. A report by Longworth et al.[6] found that the MicroFID was not sensitive enough to detect CW agents at concentrations within an order of magnitude of the Joint Services Operational Requirement (JSOR) levels for any of the conditions tested. Moreover, unpredictable detection performance made establishment of a reliable response curve impossible. While methane detection responses did not appear to be affected by relative humidity changes, CW agent detection at varied humidity conditions showed considerable variance.[6]

Figure 2: Photovac MicroFID flame ionization detector

c. *PIDs*: RAE Systems manufactures several handheld PID devices, including the MultiRAE Plus, which is currently on the AF BE 886H allowance standard. Every instrument in the MultiRAE series also incorporates a combustible gas monitor, and the MultiRAE Pro features gamma radiation detection and dosimetry as well. The RAE Systems PIDs that are reported to have the highest sensitivity are the ppbRAE (Figure 3) and the MultiRAE Pro, both of which are designed to detect contaminants in the parts per billion range. A study by Longworth and Ong[7] found that the ppbRAE could not detect GA or GB to meet JSOR levels, the National Institute for Occupational Safety and Health's (NIOSH) immediately dangerous to life and health values, or the Centers for Disease Control and Prevention's airborne exposure limit values. Two out of three ppbRAE units tested in that study were able to detect HD at the JSOR level but none were able to meet AEL detection requirements for HD. The ppbRAE exhibited a wide range of response between units, as well as within the same unit, so no meaningful response curve could be determined.[7] On the other hand, a report by Maughan et al.[4] found the ppbRAE to be both precise and accurate over most hydrocarbon concentration ranges tested. It also demonstrated the shortest response time of all five instruments tested.[4] Other PID-based COTS instruments are manufactured as well, such as the Multi-PID 2 by Draeger and the PhoCheck 5000+ by ION Science. Although no independent literature appears to have been published with regard to these devices, the manufacturers' product information does not indicate that they possess any significant advantages in capability over the ppbRAE or the TVA-1000B.

Figure 3: RAE Systems ppbRAE 3000 photoionization detector

d. *IR*: A different but related technology for analysis of gases and vapors is infrared spectrometry, which is employed by instruments such as the MIRAN SapphIRe (Figure 4). Like the PID, neither oxygen nor nitrogen interferes with IR operation, while water vapor is a major source of interference (*Final Guidance Document for Use of the Thermo Electron TVA-1000B Toxic Vapor Analyzer*; USAFSAM, 2007). Unlike the PID or FID, the SapphIRe is able to measure multiple gases or vapors in a mixed environment.[8] A study by Coffey et al.[8] indicated that the ppbRAE and the SapphIRe had similar agreement with charcoal tube measurements of hexane under all conditions. A report by Longworth et al.[9] found that, when compared to JSOR and IDLH values, the detection limits of the SapphIRe for nerve agents (GA and GB) were an order of magnitude higher. Also like the MicroFID, the baseline response of the SapphIRe was

affected by relative humidity changes. The report stated, “The usefulness of this type of detector [SapphIRe] for first responders in unknown situations is considered minimal.”[9] Table 1 is data from a study by Butler[10] that compares detection capabilities of PID, FID, and IR instruments for several chemicals of concern. Of these 52 contaminants, only 3 (carbon dioxide, carbon monoxide, and nitrous oxide) can be detected by IR but not by PID or FID.

Figure 4: Thermo Scientific MIRAN SapphIRe infrared spectrometer

3. CONCLUSIONS: Based on this review of available, relevant literature, there do not seem to be enough significant advantages in existing COTS portable gas and vapor monitoring instruments to justify replacing the TVA-1000B at this time. Because the findings in the literature do not indicate any advantages in existing COTS portable gas and vapor monitoring instruments compared to the TVA-1000B, additional performance testing of the TVA-1000B versus other comparable COTS options was not conducted as part of this review and is not recommended at this time. Perhaps future technological advances will result in portable instruments that have significantly lower detection limits or can measure a wider variety of chemicals or mixtures of chemicals compared to the TVA-1000B. If such advances do occur, the AF should then evaluate potential replacements to the TVA-1000B, using NIOSH guidance[11] for evaluation of direct-reading monitors. Until then, BE equipment modernization might be better implemented in other ways.

Table 1. Detection Capabilities of PID, FID, and IR for Some Chemicals of Concern

CAS	Chemical Name	PID	FID	IR
134-32-7	Alpha-napthylamine	+	-	-
71-43-2	Benzene	+	+	+
75-21-8	Ethylene oxide	+	+	+
50-00-0	Formaldehyde	+	+	+
62-75-9	N-nitrosodimethylamine	+	-	-
75-01-4	Vinyl chloride	+	+	+
75-07-0	Acetaldehyde	+	-	+
53469-21-9	Aroclor-1242	-	-	-
11097-69-1	Aroclor-1254	-	-	-
117-81-7	Bis-phthalate (DEHP)	-	-	-
106-99-0	1,3-butadiene	+	+	+
56-23-5	Carbon tetrachloride	+	-	+
67-66-3	Chloroform	+	-	+
72-55-9	Dichlorodiphenyldichloroethylene (DDE)	-	-	-
107-06-2	1,2-dichloroethane	+	-	-
123-91-1	1,4-dioxane	+	-	+
100-40-3	4-ethenylcyclohexene	+	-	-
106-93-4	Ethylene dibromide	+	-	-
75-02-5	Fluoroethene	+	-	-
75-09-2	Methylene chloride	+	+	+
79-46-9	2-nitropropane	+	-	-
10595-95-6	N-nitrosomethylethylamine	-	-	-
127-18-4	Tetrachloroethylene (PCE)	+	+	+
79-01-6	Trichloroethylene (TCE)	+	+	+
75-05-8	Acetonitrile	-	+	+
79-10-7	Acrylic acid	+	+	-
7664-41-7	Ammonia	+	-	+
92-52-4	1,1-biphenyl	+	-	-
84-66-2	Benzenedicaroxylic acid	-	-	-
123-72-8	Butanal	-	-	-
109-74-0	Butanenitrile	-	-	-
71-36-3	1-butanol	+	+	+
124-38-9	Carbon dioxide	-	-	+
75-15-0	Carbon disulfide	+	-	+
630-08-0	Carbon monoxide	-	-	+
57-14-7	1,1-dimethylhydrazine	+	-	-
593-74-8	Dimethyl mercury	-	-	-
104-76-7	2-ethyl-1-hexanol	-	-	-
628-73-9	Hexanenitrile	-	-	-
591-78-6	2-hexanone (MBK)	+	-	-
589-38-8	3-hexanone	-	-	-
7439-97-6	Mercury	-	-	-
75-50-3	N,N-dimethyl-methanamine	+	-	-
67-56-1	Methanol	-	+	+
60-34-4	Methyl hydrazine	+	-	-
624-83-9	Methyl isocyanate	+	-	-
10102-44-0	Nitrogen dioxide	+	-	-
10024-97-2	Nitrous oxide	-	-	+
110-59-8	Pentanenitrile	-	-	-
128-37-0	2,6-bis-4-methylphenol	-	-	-
107-12-0	Propanenitrile	-	-	-
126-73-8	Tributyl phosphate (TBP)	-	-	-

NOTE: "+" symbol indicates instrument is capable of detecting chemical

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5. Thank you for affording USAFSAM/OEC the opportunity to assist you. Please direct additional questions to Capt Jason Flory, DSN 798-3860, or jason.flory@wpafb.af.mil.

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